

Doklady Akad.Nauk SSSR 66, 561-4  
(1949)

VELOCITY OF REDUCTION OF MANGANESE OXIDES  
BY HYDROGEN AND BY CARBON MONOXIDE

By

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This work deals with the investigation of rates of reduction of  $MnO_2$ ,  $Mn_2O_3$  and  $Mn_3O_4$ , with carbon monoxide and show comparison of the rates of reduction of above mentioned oxides of manganese with hydrogen and with carbon monoxide.

In each test the starting material consisted of a sample of an oxide of manganese, a duplicate of which was used earlier in test reductions with hydrogen. Each one of these samples had a previously determined surface.

The method, apparatus and conditions of each test were exactly duplicate of the previous work and thus the results obtained on the test reduction of manganese oxides by hydrogen and by carbon monoxide are easily comparable.

A one gram sample of an oxide was used in each test and the determination was carried out in a closed system with circulating carbon monoxide. The effluent gas products were passed through a liquid nitrogen cooled cold trap to fixate and the carbon dioxide. The rates of reduction were determined from the drop in pressure in the system during known time increments. The tests were carried out at initial carbon monoxide pressures of 50, 100 and 200 mm Hg at 30° intervals in the 350-500°C temperature range.

The reduction of oxides of manganese either with hydrogen or with carbon monoxide under the above mentioned conditions of temperature and pressure proceeds easily to the  $MnO$  stage, and for convenience the reduction to the  $MnO$  stage, was taken as 100%.

Reduction of  $MnO_2$

Experimental data pertaining to reduction of  $MnO_2$  are shown in Figure 1, which shows the rate of reduction as a function of hydrogen or carbon monoxide pressure at constant temperature with the oxygen content of solid phase shown on the curves as percentage reduction. Similar relationships were also obtained at other temperatures under investigation. As shown in Figure 1, reduction of  $MnO_2$  is considerably more rapid with carbon monoxide than with hydrogen. Also is of note the different character of relation between the rate of reduction and pressure of the reducing gas. In case of hydrogen, with the decrease in pressure, while in case of carbon monoxide the exponential nature of the relationship between change in pressure and rate of reduction is noted. The apparent activation energies, calculated from kinetic data are 16.2 Kcal/mole for reduction of  $MnO_2$  by carbon monoxide, and 24.0 Kcal/mole for reduction of  $MnO_2$  by hydrogen.

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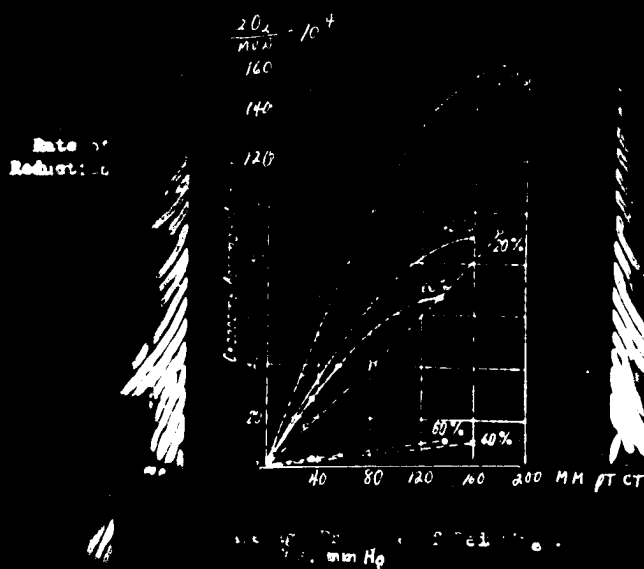


Figure 1

Influence of pressure on rate of reduction of  $MnO_2$  by carbon monoxide (1) and by hydrogen (2) at  $450^\circ C$  and constant oxygen content in solid phase.

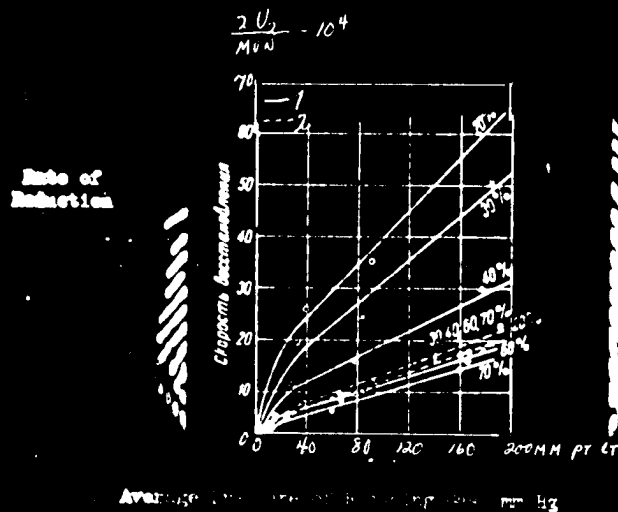
#### Reduction of $MnO_2$

The autocatalytic character of  $Mn_2O_3$  reduction by carbon monoxide was detected in a series of tests carried out at low pressures of the reducing gas (about 0.5 mm Hg) and only in the beginning stages of development of the active surface (on the  $Mn_2O_3$  sample).

This difference in the behavior of  $Mn_2O_3$  towards the reducing gas is shown in Figure 2, in which the rate of reduction or by carbon monoxide is plotted as a function of the pressure of reducing gas at constant temperature and constant oxygen level (content) in the solid phase. It can be seen from Figure 2 that the rate of reduction of  $Mn_2O_3$  with carbon monoxide is greater than with hydrogen at low conversion percentages. At higher conversion percentages (above 40%) the rate of reduction with hydrogen becomes greater. This is connected with the differential reduction of  $Mn_2O_3$  to  $Mn_3O_4$  in the first part of the reduction process and further reduction of  $Mn_3O_4$  to  $MnO$  in the latter stages of the overall reduction process, with  $Mn_3O_4$  acting quite differently towards the reducing gas.

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The apparent energy of activation for reduction of  $Mn_2O_3$  by carbon monoxide was determined to be 28.0 Kcal/mole and 22.0 Kcal/mole for reduction of  $Mn_2O_3$  by hydrogen.



**Figure 2**

Influence of pressure on rate of reduction of  $Mn_2O_3$  by carbon monoxide (1) and by hydrogen (2) at 450°C and constant oxygen content in solid phase.

#### Reduction of $Mn_2O_3$

Differing from the other two oxides of manganese, the reduction of  $Mn_2O_3$  proceeds slower with carbon monoxide than it does with hydrogen. Figure 3, the experimental data show the dependence of the rate of reduction of this oxide on the reduction gas pressure at constant temperature and at constant oxygen content in the solid phase. It can be seen from Figure 3 that the character of dependence of the reaction rate on the gas pressure is similar for both the carbon monoxide and for hydrogen, but, for a given oxygen content of the solid phase, the reduction of  $Mn_2O_3$  proceeds faster with hydrogen than with carbon monoxide.

The apparent activation energy for the reduction of  $Mn_2O_3$  was found to be 25.5 Kcal/mole for carbon monoxide and 22.0 Kcal/mole for hydrogen.

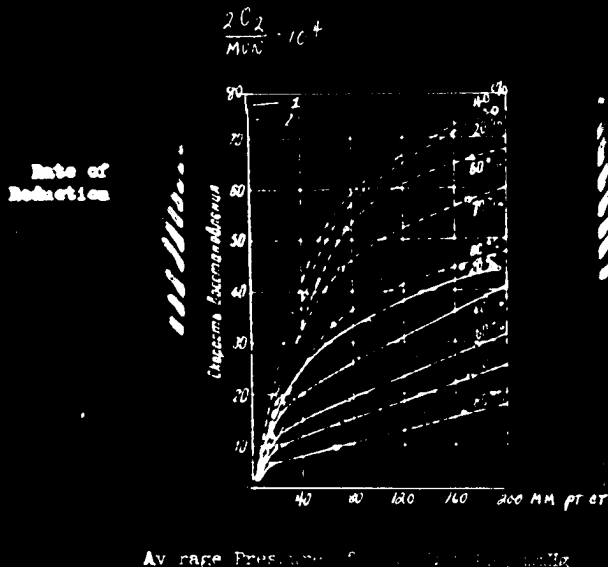


Figure 3

Influence of gas pressure on the rate of reduction of  $Mn_2O_3$  by carbon monoxide (1) and hydrogen (2) at 500°C and at constant oxygen content of solid phase.

The above presented experimental data show a different behavior of the three oxides of manganese towards the reducing gases and does not support the widespread opinion that carbon monoxide is in all cases a poorer reducing agent than hydrogen. This different behavior of manganese oxides toward the two reducing agents supports the catalytic adsorption mechanism theory of reduction of metallic oxides. With better adsorption of molecules of a given reducing agent and with a more favorable configuration (distribution) of these molecules on the surface of the oxide, the rate of reduction of oxide would be greater, since it is determined by the surface reaction, if the process is not limited by diffusion of the reducing agent to the active surface and the decidedly slowing influence of gaseous products of the reaction is absent. These two latter conditions were fulfilled in the above described experimental work.

The different rates of reduction of manganese oxides by hydrogen and by carbon monoxide correspond to different values of the apparent activation energies, but not in all cases the lower energy values corresponds to the greater rates of reduction, as for example, in case of  $Mn_2O_3$  the reverse is true. This may be due to a greater magnitude of the pre-exponential factor in the absolute reaction rate expression.

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Literature:

1. E.P. Tatievskaya, V.K. Antonov and G.I. Chufarov, Academy of Science News, SSSR No. 3, 371 (1948)

Translated by:  
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4/29/57  
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